SINTEF Building and Infrastructure   Thale Sofie Wester Plesser

Effect of surface treatment on chloride ingress and carbonation in concrete structures – State of the art

COIN Project report 3 - 2008

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COIN P4 Operational service life design

SP 4.5 Preventive measures

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Summary

The durability of reinforced concrete structures depends strongly on the durability of the steel reinforcement. Surface treatment of concrete or steel reinforcements provide a means to prevent reinforcement corrosion. The report is a literature review and is based on articles found in scientific literature as well as books that are published on the subject. The focus is on surface treatment of newly constructed structures, rather than repair systems.

The review revealed the following research needs:
- Improved and more thorough ways to classify and characterize service environments.
- Laboratory tests that are designed so that they can be related to in-field use.
- Studies that show the relation, if any, between initial properties and long term properties of a surface treatment.
- In depth investigations of the mechanisms by which surface treatments fail.

Oslo, 2008

Tor Arne Hammer   Thale Sofie Wester Plesser
Centre Manager

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.coinweb.no

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1 Introduction

The durability of reinforced concrete structures depends strongly on the durability of the steel reinforcement. Conventional carbon steel concrete reinforcement is subject to corrosion in specific environments.

In this report the focus will be on the surface treatment of newly constructed structures with the aim of preventing reinforcement corrosion, rather than repair systems. The report is a literature review and is based on articles found in scientific literature as well as books that are published on the subject.

1.1 Corrosion mechanism

Steel corrosion is an electrochemical process with an anode and a cathode reaction (Metha and Monteiro 2006):

$$\text{Anode reaction:} \quad Fe_{(s)} \bullet Fe^{2+} + 2e^{-} \tag{1}$$
$$\text{Cathode reaction:} \quad 1/2\ O_2 + H_2O + 2e^{-} \bullet 2(OH)^{-} \tag{2}$$
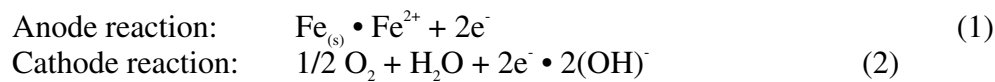
Iron ions, hydroxide and oxygen reacts to form a mixture of solid compounds, which constitute rust: $Fe(OH)_2$, FeO, $Fe(OH)_3$, the black Fe_3O_4 and the red-brown $Fe_2O_3 H_2O$. The corrosion products have a much larger volume than the original metal, causing the concrete to crack and spall.

1.2 Carbonation

In a sufficiently alkaline environment, carbon steel is protected against corrosion by a passivating layer of iron oxide. The thickness of the iron oxide layer is 2-20 nm (Nürnberger 2007). In the absence of chloride ions the oxide film will remain stable when the pH of the pore water remains above 11.5. When the pH falls below 9.0 severe corrosion starts. The process of carbonation lowers the pH in the porewater of the concrete. The carbonation process starts at the concrete surface and proceeds inwards, producing a carbonation front. Gaseous carbon dioxide from the air dissolves in the concrete pore water, dissociates and reacts with hydroxide ions (Glasser et al. 2007):

$$CO_{2(aq)} + 2\ OH^{-} \bullet CO_3^{2-} + H_2O \tag{3}$$

The carbonate ions react with dissolved calcium ions leading to the formation of calcium carbonate, mainly as calcite:

$$Ca^{2+} + CO_3^{2-} \bullet CaCO_{3(s)} \tag{4}$$

The source of calcium and hydroxide ions is $Ca(OH)_2$ (portlandite) in the concrete. When the calcium hydroxide is consumed the pH of the pore water is reduced until it eventually drops below 9.0. The portlandite is replaced by calcite, which has a higher molar volume, and the porosity of the material is reduced.

Carbonation by diffusion of carbon dioxide from the concrete surface and inwards is a relatively slow process, dependent on the concrete permeability. The maximum rate of carbonation is reached at 50-70 % relative humidity in the concrete (Bamforth 2004). At high relative humidity carbon dioxide is unable to penetrate into the concrete and at low relative humidity the carbonation reaction cannot proceed due to lack of water. The rate increases with increasing temperature and carbon dioxide partial pressure in the air. Cracks in the concrete cover allows carbon dioxide easier access and the carbonation front will reach the reinforcment faster.

1.3   Chloride ingress

The protective passivating layer of oxide on steel reinforcements can be destroyed by chloride ions when the chloride concentration in the vicinity of the steel surface reaches the chloride threshold (Glasser et al. 2007). Pitting corrosion is concentrated to a small area of the steel, but can affect the entire cross-sectional area of the reinforcement and thus cause collapse of the structure (Basheer et al. 2001). General corrosion has a homogeneous distribution that may lead to higher total loss of iron than pitting corrosion, but is still considered less dangerous. Important sources of chlorides are deicing salts used on roads and sea water in marine environments. The threshold value of chloride in the cement depends on the concrete blend and environmental conditions, but for engineering purposes a value of 0.4 % per cement weight is accepted as giving minimal risk of corrosion.

The chloride is bound in the cement paste or exists as free ions in the pore solution. Chloride is primarily bound as Friedl's salt ($3CaO^.Al_2O_3^.CaCl_2.10H_2O$), but other compounds are also possible (Glasser et al. 2007). Fixed chlorides do not contribute to corrosion (Basheer et al. 2001), but the chlorides in the cement paste are in chemical equilibrium with chloride ions dissolved in the pore water. Additionally, carbonation of the concrete causes release of chlorides from the solid phase into the pore water, a process which may contribute to the corrosion.

Chlorides are transported into concrete by water entering through cracks in the concrete, through capillary absorption of water into the concrete capillaries and through diffusion of free chloride in the pore solution due to concentration gradients (Bamforth 2004). The transport mechanism depends on the humidity of the concrete, such that in relatively dry concrete capillary absorption dominates, whereas in wet concrete diffusion dominates (Basheer et al. 2001). In concrete containing cracks that combine to form a path through the concrete, eventually reaching the reinforcement, flow through the cracks is the dominating mechanism.

The corrosion rate depends on chloride content in the concrete, the moisture state of the concrete and the temperature (Bamforth 2004). At low relative humidities corrosion is hindered by the low resistivity and at high relative humidities the corrosion rates drop because of low oxygen levels. Maximum corrosion rates occur at a relative humidity of about 95 %.

2   Preventive systems

A mixture of methods are employed for controlling corrosion (Bamforth 2004). These include concrete composition (low water/binder ratio), design and work procedures that minimizes cracking, ensures good curing of the concrete and sufficient concrete cover. The methods for controlling corrosion also include corrosion inhibitors, coatings and other surface treatments for the concrete surface as well as the reinforcement bars.

2.1   Treating the concrete surface

The surface treatments aim at keeping one or more of the necessary constituents in the depassivating process and/or corrosion reactions from entering the concrete (Janz and Byfors 2004). Protection against carbonation is usually achived by treating the surface with a coating that has limited carbon dioxide permeability or by treating the surface with a material that absorbs carbon dioxide. Protection against chloride ingress is usually achieved by preventing absorption of water. In order to achieve good protection it is important that the coating remains intact under the influence of factors that may lead to it's deterioration. An efficient system for protective surface treatment of concrete is generally recognized to meet the following properties (Stadelmann 2002):

- High water vapor permeability
- Low carbon dioxide permeability
- Low liquid water absorption
- Good adhesion to the substrate
- Good retention of properties on ageing (UV-stability, resistance to temperature changes).
- Good crack bridging ability
- Good resistance to alkalis

Controlling the ingress of liquid water into concrete is particularly important for two reasons: First, because without water the carbonation reaction or the cathode reaction (eq. 2) could not take place. Second, because water helps transport aggressive substances like carbon dioxide and chloride into the concrete. The carbonation rate of concrete has been found to correlate well with the short term absorption of water (Basheer et al. 2001). Low water-absorption also correlates well with low chloride permeability (Basheer et al. 2001 and Al-Zahrani et al. 2002). A coating with low water absorption prevents water from being absorbed by the concrete, and high water vapor permeability allows water that has been trapped behind the coating to evaporate. A coating with good crack-bridging ability will prevent water from entering through existing and developing cracks in the concrete.

Performance criteria for protective surface treatments are set down in EN 1504-2:2005 "*Products and systems for the protection and repair of concrete structures. Definitions, requirements, quality control and evaluation of conformity. Part 2: Surface protection systems for concrete*". A summary of the requirements are given in table 1 and 2. These requirements are no guarantee that the products give sufficient protection in all environments.

As can be seen from table 1, there are no requirements or test methods specified for chloride ion permeability, but EN 1504-2 states that when the capillary absorption of water is lower than 0.01 $kg/(m^2 \ h^{0.5})$ the diffusion of chloride ions is not to be expected. Carneiro et al. (2006) has suggested that it may not always be sufficient to prevent water absorption as chloride ions are transported through the coating film dissolved in water or by an ion exchange mechanism. When the ion exchange mechanism dominates or contributes sufficiently to the chloride transport it is necessary to determine the chloride permeability by direct measurement.

Table 1. Requirements for hydrophobic impregnations used for the protection of concrete surfaces, according to European standard EN 1504-2.

Property	Test method	Requirements
Loss of mass after freeze-thaw-salt stress	EN 13581	The loss of mass in an impregnated specimen must occur at least 20 cycles after the loss of mass is observed in the not impregnated specimen
Depth of penetration of the hydrophobic impregnation	prEN 14630	Class I: < 10 mm Class II: • 10 mm
Water absorption and resistance to alkali	EN 13580	Absorption ratio < 7,5% compared with the untreated specimen Absorption ration after immersion into alkali solution < 10%
Drying rate coefficient	EN 13579	Class I: > 30% Class II: > 10%
Diffusion of chloride ions	Subject to national standards	No requirements specified in EN 1504-2 but when the capillary absorption of water is lower than 0.01 kg/(m^2 h$^{0.5}$) the diffusion of chloride ions is not expected.

Table 2. Requirements for impregnations and coatings used for the protection of concrete surfaces, according to European standard EN 1504-2.

Property	Test method	Requirements	
		Impregnation	Coatings
Permeability to water vapor, [m]	EN ISO 7783-1 EN ISO 7783-2	Class III (permeable): $S_d <$ 5	Class III (permeable): $S_d <$ 5
Capillary absorption of water, [kg/(m^2 h$^{0.5}$)]	EN 1062-3	w < 0.1	w < 0.1
Adhesion (pull-off), [N/mm^2]	EN 1542	Vertical: • 0.8 Horizontal without trafficking: •1.0 Horizontal with trafficking: • 1.5	Rigid systems without trafficking[1]: •1.0 Rigid systems with trafficking: • 2.0 Flexible systems without trafficking[1]: •0.8 Flexible systems with trafficking: • 1.5
Adhesion to wet concrete, [N/mm^2]	EN 13578		•1.5. No blistering, cracking or flaking.
Permeability to CO_2, [m]	EN 1062-6	-	$S_d >$ 50
Crack-bridging ability	EN 1062-7	-	Class A5[2]: > 2,5 mm
Chloride permeability	Subject to national standards	-	No requirements specified in EN 1504-2 but when the capillary absorption of water is lower than 0.01 kg/(m^2 h$^{0.5}$) the diffusion of chloride ions is not expected.

1) Rigid system: Shore D • 60 according to EN ISO 868.
2) Test method A, continuous opening of the crack.

A number of systems exist for the treatment of concrete surfaces. Commercial treatment systems often consist of a combination of two or more generic types. It must be pointed out that large differences can exist between two products within the same generic type. The general descriptions given for each treatment type in the following text hold true for properly formulated products aimed at the treatment of concrete surfaces, but are not necessarily true for all products of the same type.

2.1.1 Acrylic and styrene-acrylic copolymer coatings

Acrylic and styrene-acrylic copolymers have the general chemical structure shown in figure 1. These coatings are characterized by good resistance to mild alkalis, good adhesion, high water vapor permeability, low carbon dioxide permeability, low water absorption and good crack-bridging ability (Stadelmann 2002). Styrene confers greater hydrophobicity to the film, but contains double bonds that detract from the stability towards ultraviolet light. The acrylates show good chemical resistance to mild alkalis but the ester linkage is vulnerable to attack by stronger alkalis which can cause problems if the coating is applied on a young concrete.
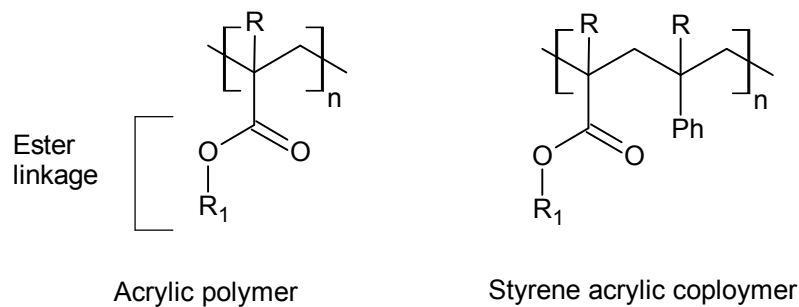
Figure 1. The general chemical structure of acrylic and styrene-acrylic copolymers. The R in the main chain of the polymer is typically a methyl (methacrylate polymer) while the R_1 on the side chain typically is methyl or butyl. The "Ph" in the styrene acrylate denotes a phenyl group.

A wide selection of acrylate-based coatings is commercially available. Decorative coatings that protect against carbonation are most often acrylic latexes. These coatings are produced by emulsion polymerization of various acrylate and acrylic acid monomers (Wicks et al. 2007, p. 186).

Several studies confirm the ability of acrylic-based coatings to protect concrete structures against water ingress, chloride induced corrosion and carbonation in urban and marine environments (Ibrahim 1997, Seneviratne et al. 2000, Uemoto et al. 2001, Almusallam et al. 2003, and Batis et al. 2003), see table 3. However, the studies are mostly based on commercially available products, and very little is known about the composition of the coatings. All that can be concluded about acrylic coatings on the basis of these studies is that they perform well although particular coatings of other generic types sometimes perform better.

Table 3. Accelerated tests comparing the ability of coatings to prevent reinforcement corrosion. The table is based on data from Ibrahim et al. (1997). The water-cement ratio of the concrete equals 0.45 and the concrete contains 350 kg/m^3 of cement.

Treatment	Time to cracking[1] [h]	Time until the corrosion is initiated[2] [days]
Uncoated	144	10
Sodium silicate	176	12
Silicon resin solution	200-300	40
Silane/Siloxane	2125	55
Alkylalkoxysilane	> 4350	340
Silane/siloxane with acrylic top coat	> 4350	225
Two component cement-based acrylic coating	> 4350	320

1) The specimens were partially immersed in 5 % sodium chloride and a 2 V potential was applied to accelerate the process.
2) The specimens were partially immersed in 5 % sodium chloride and the corrosion potential was measured. ASTM C 876 specifies that reinforcement corrosion is initiated when the corrosion potential drops below -270 mV.

2.1.2 Polymer-modified cement coatings

Cement coatings contain cement, sand, and additives that improve and modify the coating properties (Squirrel 2002). They can contain a wide range of polymers, e.g. acetates, styrene-butadiene rubbers, styrene-acrylics and acrylics. The coatings exhibit good adhesion, low water absorption, low carbon dioxide permeability and high durability. Reinforced products have good crack-bridging abilities. The addition of cross-linked acrylics can improve the performance even more (Boodaghians 2002).

2.1.3 Epoxy resin coatings

Epoxies are two-component coatings usually made from an epoxy resin based on bisphenol-A and/or bisphenol-F and epichlorohydrin, and a hardener or cross-linker, usually an amine (Beinborn and Darwen 2002), see figure 2. The hardener and the epoxy resin form a crosslinked network. A large range of amine hardeners are available each type imparting specific characteristic properties to the final product. Phenols, carboxylic acids and anhydrides can also make efficient cross-linkers (Wicks et al. 2007 p. 286).

Epoxy resins have good chemical resistance, high water vapor permeability and low water absorption. Flexible formulations have good crack-bridging ability. Epoxy novolac resins are used when very high chemical resistance is needed.

Epoxies are often used as sealers in combination with polyurethane top coats, but systems consisting entirely of epoxies are also used. Environmental concerns have prompted research into reducing the solvent emissions from paints, and have led to the development of solvent-free formulations. Studies comparing epoxy coatings with coatings systems of other generic types show that epoxy coatings perform well in accelerated testing schemes, but products must nevertheless be evaluated individually irrespectively of generic type (Al-Zahrani et al. 2002, Almusallam 2003). However, epoxy systems are subject to blistering (Al-Zahrani et al. 2002).

Bisphenol A epoxy resin
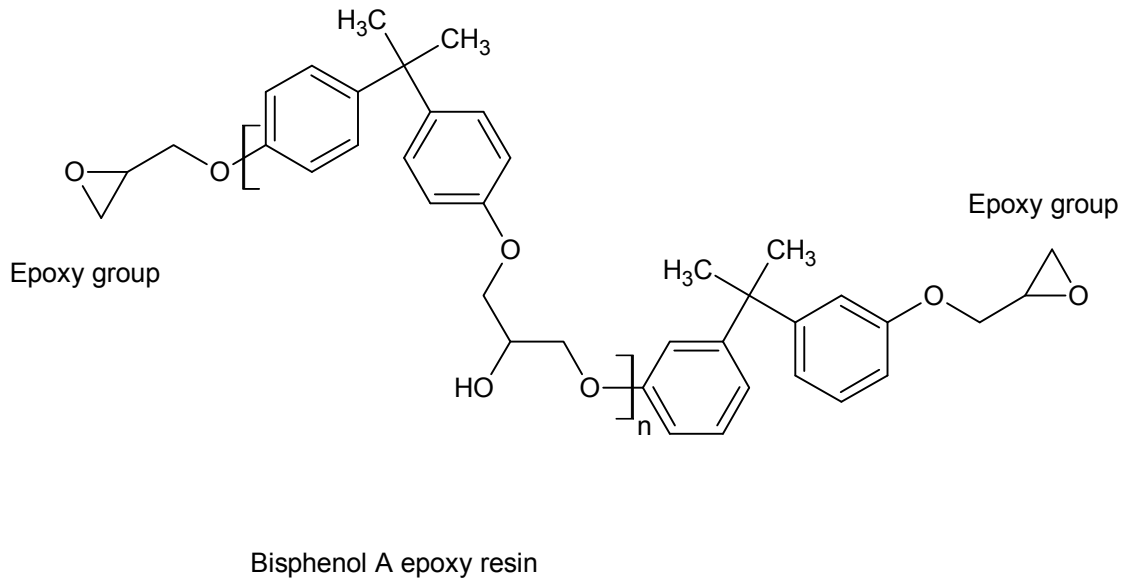
Figure 2. Bisphenol A epoxy resins find many commercial applications. The epoxy group at the end of the epoxy resin reacts with the hardener and a crosslinked network is formed.

2.1.4 Polyurethane resin coatings

Polyurethanes are made by reacting an isocyanate with an alcohol or water (Wilson 2002), see figure 3. A very wide range of products and coatings can be produced in this way. The isocyanates can be divided into two groups, aliphatic and aromatic. Examples of isocyanate monomers are hexamethylene di-isocyanate (HDI) and methylene diphenyl di-isocyanate (MDI), see figure 4. HDI is aliphatic and MDI is aromatic. Common types of polyols can be divided into one of the following groups: polyester polyols, polyether polyols, polycarbonate polyols and polyacrylate polyols. The effect of polyurethane polyol and isocyanate constituents on some polyurethane properties are outlined in table 4.
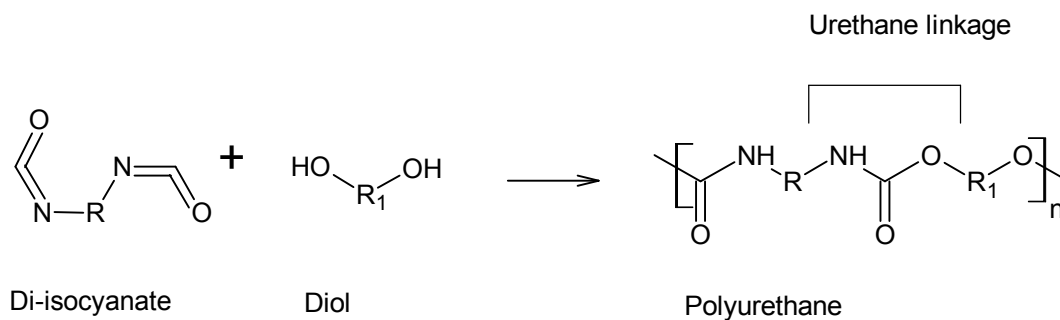
Figure 3. Example of how a polyurethane is formed.
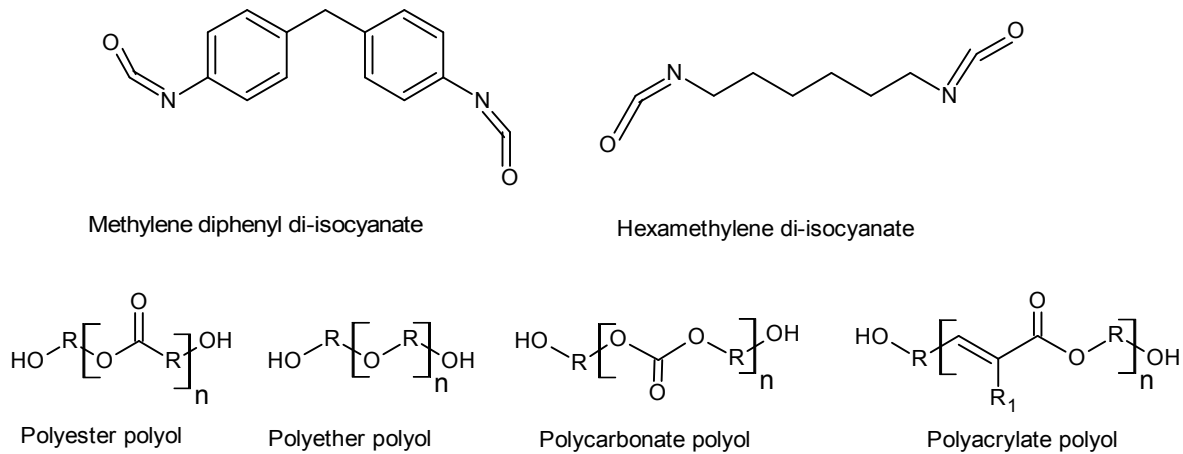
Figure 4. Examples of commonly used di-isocyanate monomers and polyols.

Table 4. The effect of polyurethane polyol and isocyanate constituents on some polyurethane properties (Wilson 2002).

Constituent	Chemical resistance	Weathering resistance	Flexibility	Hardness	Abrasion resistance	Heat resistance	Water resistance
Aliphatic isocyanate	Good	Excellent	Good	Good	Good	Good	Very good
Aromatic isocyanate	Excellent	Poor	Fair	Excellent	Excellent	Very good	Excellent
Polyester polyol	Fair	Good	Excellent	Fair	Good	Poor	Good
Polyether polyol	Fair	Fair	Excellent	Poor	Poor	Poor	Fair
Polycarbonate polyol	Fair	Good	Excellent	Fair	Good	Fair	Good
Polyacrylate polyol	Good	Excellent	Good	Good	Good	Good	Good

Adhesion of polyurethanes to concrete is usually good but can be a problem on wet substrates (Vipulanandan and Liu 2005). A correctly formulated polyurethane has good crack-bridging ability and low carbon dioxide permeability.

Polyurethanes are most commonly of the two-component type. One component is a polyol (an organic compound containing two or more reactive hydroxyl groups) and the other a polyisocyanate prepolymer. The two components are mixed shortly before application and the components react to form polyurethane. The reaction is moisture sensitive because water acts as a competitor to the polyol. This can lead to reduced coating performance. Moisture cure polyurethane systems utilize water as curing agent. As a result of environmental awareness, as well as concern for health and safety, water-based polyurethanes have been introduced. The water-based systems can be both single-pack and two-component.

Polyurethane top-coats are often used in combination with primers or sealers: moisture cure polyurethanes, acrylics, epoxies or silanes/siloxanes. A correctly used primer or sealer promotes adhesion and may also add to the waterproofing ability of the system.

Several comparative studies confirm that polyurethanes and systems with a polyurethane component perform well in accelerated corrosion tests compared to other coating systems (Zhang and Buenfeld 2000, Al-Zharani et al. 2002, Almusallam 2003).

2.1.5   Products based on silicon

Surface treatments based on the chemical element silicon include silanes, siloxanes, silicone resins and silicate paints (Thomas 2002). The basic unit is silicon which is tetrahedrally bonded to oxygen or an alkyl group. The most basic group is the alkyltrialkoxysilane also known as just silane. Reaction of alkyltrialkoxysilane with water, either prior to surface application or after application causes the siloxane to form a silanol intermediary which condenses to form an alkylalkoxysiloxane or siloxane for short (Witucki 1993), see figure 5.

$$
2 \quad \underset{\overset{|}{OR}}{\overset{\overset{OR}{|}}{R'\text{-Si-OR}}} \quad \xrightarrow[-\ 3\ ROH]{+\ H_2O} \quad \underset{\overset{|}{OH}\ \ \overset{|}{OH}\ \ \overset{|}{OH}}{\overset{\overset{R'}{|}\ \ \overset{R'}{|}\ \ \overset{R'}{|}}{OH\text{-Si-O-Si-O-Si-OH}}}
$$

Alkyltrialkoxysilane   Alkyltrialkoxysiloxan
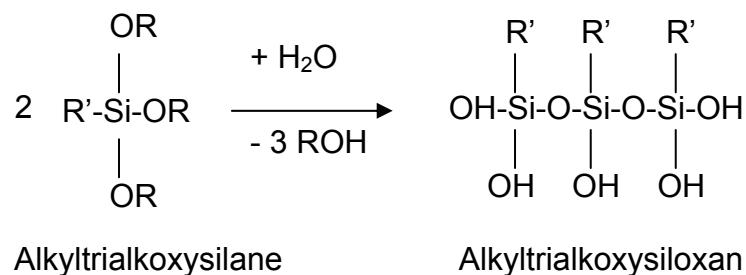
Figure 5. Alkyltrialkoxysilane reacts with water and condenses to form alkylalkoxysiloxane. Alkylalkoxysiloxane typically contains three to six silicon atoms, the siloxane shown here is the shortest variety. The R in the silane is typically a methyl or ethyl group, while possibilities for the R' include methyl, butyl or octyl.

Both silanes (alkyltrialkoxysilanes) and siloxanes (alkylalkoxysiloxane) are used as water repellants for concrete. They impart low water absorption and high water vapor permeability. Silanes and siloxanes enter easily into the concrete and are alkali resistant, but cannot prevent carbon dioxide from entering the concrete or resist water under pressure. Silanes and siloxanes are often used together with polyurethane, or epoxy top-coats. The effectiveness of silanes and siloxanes depend on their ability to penetrate into the concrete. Silanes and siloxanes react with the surface of the concrete pores, forming chemical bonds through the alcohol oxygen's. The pores remain open and water is repelled due to the hydrophobicity of the alkyl groups.

A study of several silane and siloxane products show large differences in the performance of the different products (Schueremans et al. 2007), see table 5. In this study isobutyltrialkoxysilane performed best, while methylsiloxane only gave some protection compared to the untreated concrete. Pure alkyltrialkoxysilanes penetrates easily into the concrete but they are volatile and will, even under normal application conditions, to a large degree evaporate. As a result most commercial products are mixtures of siloxanes and silanes or microemulsions (Haydn 2002). Mixtures containing alkyltriethoxysilane are particularly effective (Schueremans et al. 2007).

Table 5. Chloride penetration depth in concrete cubes treated with silane and siloxane products after 90 days of exposure. Data from Schueremans et al. (2007, figure 6).

Treatment	Chloride penetration depth [mm]
Isobutyltrialkoxysiloxane	1.5
Isooctyltrimethoxysiloxane/ isooctyltrialkoxysiloxane	9.5
Isooctylsiloxane/ methyltrimethoxysilane	11
Untreated	48

Silicone resins form three-dimensional cross-linked networks with silicon bonded to oxygen and organic groups, see figure 6. They are characterized by high water vapor permeability, low water absorption, and high carbon dioxide permeability. Some resins are vulnerable to alkali attack.
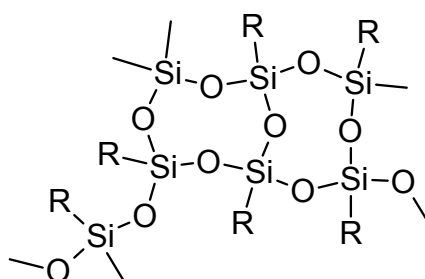
Figure 6. Silicone resin. R denotes organic substituents.

Silicate paints have high water vapor permeability, low water absorption, and high carbon dioxide permeability (Gatrell 2002). The binder is potassium waterglass. Single-pack formulations contain an acrylate copolymer as stabilizer. The composition of silicate paints is regulated in DIN 18363: "*German construction contract procedures - Part C: General technical specifications for building works - Painting - coatings works*". The binder reacts with components in the substrate and carbon dioxide from the air, forming permanent chemical bonds to the substrate. The process is termed silification. To some degree the silicate paint will also enter the concrete pores.

2.1.6   Bacterial treatment

Some bacteria have the ability to promote precipitation of carbonates and can be used to protect substrates such as limestone or concrete (Le Métayer-Levrel et al. 1999 and De Muynck et al. 2007). In the process urea or uric acid is hydrolyzed enzymatically leading to the formation of carbon dioxide and ammonia (Hammes and Verstraete 2002). Carbon dioxide and ammonia react to form carbonate that is precipitated, see eqs. 5 and 6.

$$CO(NH_2)_2 + H_2O \bullet CO_2 + 2\ NH_3 \tag{5}$$

$$2\ NH_3 + CO_2 + H_2O \bullet 2\ NH_4^+ + CO_3^{2-} \tag{6}$$

The bacteria are applied to the substrate in a nutritional solution (Le Métayer-Levrel et al. 1999). Nutritional solution without bacteria is reapplied at intervals for a period following the first application. As a result of bacterial activity calcium carbonate is precipitated on the surface of the

substrate (De Muynck et al. 2007). Comparison of specimens treated with bacterial cultures and specimens treated with conventional sealants and coatings showed that bacterial treatments reduced the water absorption significantly and performed well compared to the conventional products, see Table 6. Bacterial treatment also reduced oxygen permeability, but not as efficiently as coatings.

Table 6. Water absorption for concrete specimens treated with conventional surface treatments and bacterial cultures. The water absorption of the untreated specimen is set to 100. Data from De Muynck et al. (2007, figure 3). The tests were performed on mortar prisms made according to EN 196-1 using Portland cement (CEM I 52.5). The water-cement ration equalled 0.5.

Surface treatment	Treatment type[1]	Nutrient [2]	Water absorption - relative to the untreated specimen[3]	Oxygen permeability coefficient [$\times 10^{-16}$ m^2]
Water based acrylic primer and coating	C	-	29	0.31
Siloxane and acrylic resin	C	-	2	0.57
2 component epoxy primer and water based modified butadiene copolymer coating	C	-	15	0.34
Styrolacrylate	C	-	31	0.59
Transparent acrylate dispersion	C	-	21	0.84
Water-based acrylate	C	-	22	1.04
Silane, water based	P	-	13	0.92
Siloxane, solvent based	P	-	20	0.78
10 % siloxane-organometal solvent based	P	-	18	0.93
Oligomeric siloxane	P	-	14	0.80
Ethyl-ethoxy, solvent based	P	-	20	-
Emulsion	P	-	16	-
Siloxane	P	-	44	-
Silane/siloxane, water based	P	-	16	0.96
Siloxane/alkoxysilane	P	-	13	1.14
Silicone	P	-	84	0.97
Polycarbonate based polyurethane	P	-	15	0.48
Uerolytic mixed culture	M	NBP	33	-
Uerolytic mixed culture	M	CaAc	37	-
Uerolytic mixed culture	M	CaCl$_2$	62	-
Uerolytic mixed culture	M	NBP + CaAc	49	0.97
Uerolytic mixed culture	M	NBP + CaCl$_2$	55	1.20
Bacillus Sphaericus	B	NBP	31	-
Bacillus Sphaericus	B	CaAc	12	-
Bacillus Sphaericus	B	CaCl$_2$	15	-
Bacillus Sphaericus	B	NBP + CaAc	13	-
Bacillus Sphaericus	B	NBP + CaCl$_2$	11	1.02
Untreated specimen	-	-	100	1.53

1) C - coating, P - penetrating sealant, M - mixed uerolytic cultures, B - Monocultures of *Bacillus sphaericus*.
2) NBP - Nutrient broth powder, CaCl$_2$ - 36 g/L calcium chloride, CaAc- 51,25 g/L calcium acetate.
3) The water absorption of the untreated specimen is set to 100. The water absorption of the specimens with surface treatments is relative to the value for the untreated specimen.

2.2 Treating the surface of the reinforcement steel

The last line of defense against corrosion lies at the surface of the steel reinforcement. Coating systems for steel reinforcements comprise epoxies, metallic coatings, and cement-based coatings, but other coating types also exist, at least in the research laboratories. Fusion bonded epoxy and galvanizing are the most widely used systems for rebar coating. The rebar coatings are applied prior to the pouring of the concrete, either in a production plant or on the construction site. In the latter case the coating is applied after the rebars have been cut and bent. An efficient rebar coating must meet the following requirements:

- Resistant to damaging before and during pouring of the concrete.
- Ability to perform despite some damage to the coating as a result of handling.
- Low water permeability.
- Low permeability to aggressive substances, such as chloride.
- Good adhesion between coating and substrate and between surrounding concrete and coating.
- Good chemical resistance in an alkaline environment.

2.2.1 Epoxy coatings

Reinforcements with an epoxy coating were first used full-scale in the early 1970's. The epoxy is used in the form of fusion bonded epoxy coating, FBE. FBE is a protective epoxy based powder coating. A number of FBE coatings exist, each tailor-made for particular applications. Before application the coating consists of two components. One component is a bisphenol-A (BPA) based epoxy resin and the other component is a hardener, normally an amide (Wicks et al. 2007, p. 550). Epoxy coatings are good corrosion protectors and have good adhesion, however, the exterior durability is poor.

The epoxy is thought to work as a physical barrier, preventing aggressive substances from coming in contact with the reinforcement, and as an electrochemical barrier by increasing the electrical resistance between neighboring steel locations where the cathodic and anodic reactions take place (Py et al. 2000, Darwin and Scantlebury 2002).

Some concern has been raised about the effectiveness of epoxy coatings. A field-performance study of bridges built in Virginia between 1977 and 1995 using epoxy-coated rebars to protect against chlorides, showed that the epoxies debonded from the steel bars in as little as four years. The coating debonded before the chlorides reached the reinforcements, probably because water had penetrated the coating and accumulated at the metal-coating interface (Py et al. 2000). The examined rebars were in good condition, but the study raised the question of what consequences damages and loss of adhesion would have on the effectiveness of the coatings once chloride ions had penetrated to the rebar depth.

Accelerated tests of epoxy coated rebars with 3 mm diameter holidays (Darwin and Scantlebury 2002) showed that no corrosion took place under the laboratory conditions. In their study, Darwin and Scantlebury subjected the specimens to monthly wet/dry cycles in 3.5 % NaCl solution over a time period of one year. These are considered severe test conditions. Some delamination of the coating was observed around the holidays, but no sign of corrosion. Results from other studies also show that the epoxy coating is capable of giving increased corrosion protection under conditions that severely corrode untreated rebars, even though there are holidays in the coating (Erdoğdu et al. 2001 and Elleithy et al. 1998).

Work is being performed on improving the epoxy coatings. Interpenetrating network polymers (IPN) are made up of two polymers that are polymerized separately from the same batch, leading to intertwined network of the polymers. Asthana et al. (1999) have performed accelerated corrosion tests (80 cycles: 1 day in 3 % NaCL solution, 3 days at 27 ± 2 °C and 3 days at 60 °C)

on IPN coated rebars and compared these to the performance of epoxy coated rebars. They found that the IPN coated rebars loss less weight due to corrosion than the fusion bonded epoxy coated rebars. The IPN was produced from an epoxy resin based on diglycidyl ether of bisphenol A as the one polymer and a phenolic resin from cashew nut shells as the other polymer. In effect, part of the epoxy resin is replaced by an inexpensive by-product from the cashew-industry. Field studies using IPN coated rebars in a natural marine environment (Gulf of Mannar, India) showed that the IPN coated rebars performed at least as well as normal epoxy coated rebars during the 1 year exposure period (Venkatesan 2006).

2.2.2 Metallic coatings

Galvanized steel bars have been used for reinforcing concrete in exposed surfaces in aggressive environments since the early 1950's. The reinforcements are coated with a thin layer of zinc through a process called hot-dip galvanization. The steel is dipped in a molten bath of zinc and metal additives. Zinc reacts with the substrate and several Zn/Fe products are formed (Gowripalan and Mohamed 1998). The zinc layer works as a sacrificial anode, i.e. it corrodes in preference to steel. The zinc layer also works as a barrier against chlorides, increasing the chloride threshold for corrosion initiation, and it has a higher tolerance of lower pH due to carbonation than steel.

The traditional zinc bath contains lead as additive. Due to environmental concerns about the use of lead, research is being performed on alternative additives (nickel, tin and bismuth) and the effect of these on the corrosion behavior of galvanized steel embedded in concrete (Bellezze et al. 2006).

Singh and Gosh (2006) suggested that electroless nickel-phosphorus (ENP) coatings may be used as an alternative metallic coating for stainless steel bars in concrete. They tested the corrosion rate of steel bars coated with medium and high phosphorus content ENP in synthetic pore solutions with dissolved sodium chloride, and found that ENP protects the steel against corrosion through the formation of a passive, pore-free Ni_2O_3/Ni_5P_2 layer. A major drawback for ENP coatings, seen from a commercial view-point, is the low deposition rate compared to other coating types.

2.2.3 Cement-based coatings

Cement-based coatings include inhibited cement slurry coatings and cement-polymer composite coating systems (CPCC). Cement-based rebar coatings are less common than fusion bonded epoxy coated rebars, but has found use in several projects on the east and west coasts of India (Vedalakshmi et al. 2000).

Inhibited cement slurry coatings are applied on-site after cutting and bending of the steel reinforcements. The application is performed in four steps (Vedalakshmi et al. 2000):

1. Removal of rust layer.
2. Phosphating.
3. Application of two coats of inhibited cement slurry coating. The inhibitor is nitrite based.
4. Silicate based sealer.

The cement-polymer composite coating system is applied either at a factory or on-site (Protekol Anticorrosives n.d.). CPCC is a polyacrylic and polyquinone modified cement (Technology offers from CECRI n.d.). A number of similar systems exist for concrete repairs, but they are not used for rebar coating in new constructions.

A study comparing CPC coated rebars with interpenetrating polymer network (IPN) coated rebars and epoxy coated rebars in a natural marine environment (Gulf of Mannar, India) showed that

CPCC performed at least as well as the other coatings during the 1 year test period (Venkatesan et al. 2006).

2.2.4 Other rebar coatings

Acrylic modified cementitious coatings and acrylic coatings for the concrete surface are used as a means to control reinforcement corrosion (Stadelmann, 2002). Wang et al. (1998) published a study on the effect of coating the rebar with a water-based methacrylate-butyl methacrylate coating. An accelerated corrosion test was perfomed on concrete specimens with coated and uncoated rebars for 60 days and showed that acrylic latex coatings reduced the corrosion rate of steel rebars.

3 Long term performance of surface treatments

Coatings that are used outdoors are subject to weathering and will eventually degrade. The main factors influencing degradation are ultraviolet radiation from the sun, heat and temperature fluctuations, moisture, atmospheric pollutants and mechanical stresses (Andrady et al. 2007). The deterioration process is complex as it depends on the binder material itself, other coating constituents and the ability of the coating additives to protect the coating. The complex interactions between the painting components and between the coating and the environment are difficult to predict and often poorly understood.

3.1 Chemical ageing - mechanisms

The most important factor contributing to polymer degradation on outdoor exposure is UV radiation. The effect of UV radiation is made more severe at higher temperatures and in some cases also by the presence of water (Andrady et al. 2003). Photooxidation, that is light induced reactions between oxygen and a material, is hindered by the addition of UV radiation absorbers and photoantioxidants to the coatings, but the protection is not perfect as the additives themselves are also subject to degradation.

Materials containing conjugated double bonds are particularly sensitive to photooxidation (Pospíšil and Nešpurek 2000). Such materials include polyurethanes and epoxies. Acrylates do not contain conjugated double bonds and are as a consequence less sensitive although not impervious to photooxidation. In acrylates and other polymers without conjugated double bonds UV induced degradation is linked to light-absorbing impurities and structural inhomogeneities. The absorption of UV radiation causes the breaking of a polymer bond resulting in a free radical that reacts with atmospheric oxygen. In a chain of reactions new radicals are formed that attack the polymer chain. Hydroperoxides and hydroperoxide radicals perform an important role in the reaction mechanisms. Heat and the presence of metal ions may trigger a similar reaction scheme. The precise mechanisms depend on the particular chemical structure of the polymer, but also on curing history and manufacturing process (Pospíšil and Nešpurek 2000).

3.1.1 Degradation of acrylates

UV radiation causes chain scission in acrylate binders (Allen et al. 1996). The degradation mechanism depends greatly on the type of acrylate. Poly(methyl methacrylate) eventually decomposes to low molecular weight species, whereas poly(methyl methacrylate co-butyl acrylate) forms short chain fragments and crosslinks.

The ester linkage in acrylates is sensitive to hydrolysis, i.e. reaction with water (Harper and Petrie 2003 p. 269). In an alkaline environment, e.g. in contact with moist concrete, the ester linkage can be broken leading to the formation of the salt of a carboxylic acid and an alcohol. The process is termed saponification.

3.1.2 Degradation of epoxies

Epoxy resins are sensitive to UV-light, a characteristic that reduces their performance outdoor (Malshe and Waghoo 2004a). Despite their sensitivity to photooxidation amine-cured epoxies are used extensively in exterior coatings. Epoxy resins absorb at about 300 nm resulting in chain scissoring, crosslinking and eventual chalking. Pigments that absorb in the same UV region contribute to the degradation reaction. Additives are used to improve the UV stability, but UV stability can also be improved by modifying the epoxy resin with linear long chain dicarboxylic acids (Malshe and Waghoo 2004a, 2004b), see figure 7. The improvement increased with the length of the chain of the acid: sebacic acid > azelaic acid > adipic acid > succinic acid > malonic acid. Converting the epoxy to an epoxy-ester improved the UV stability even more (Malshe and Waghoo 2006).
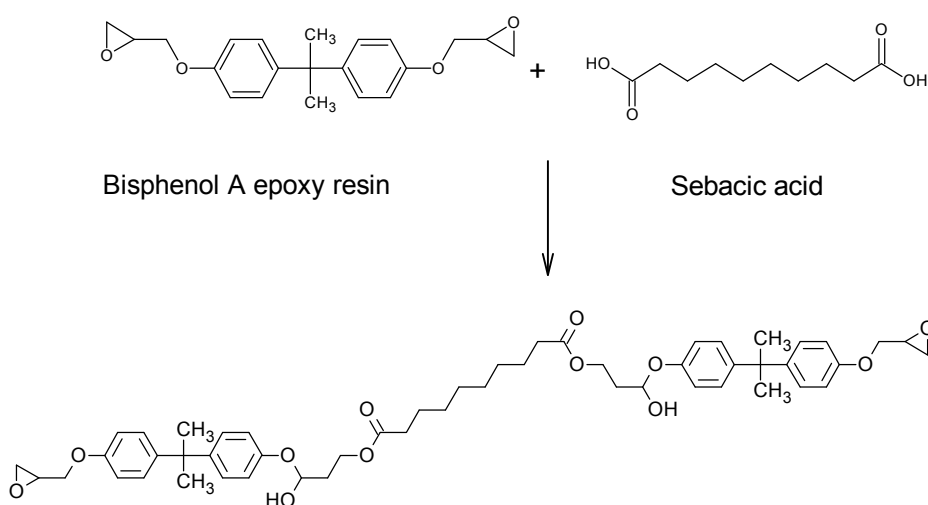

Figure 7. Reaction of a diglycidyl ether of a Bisphenol A epoxy resin with sebacic acid to form a modified epoxy resin.

Epoxies containing ester linkages are sensitive to alkaline hydrolysis as described for acrylates (Harper and Petrie 2003 p. 269).

3.1.3 Degradation of polyurethanes

UV radiation causes MDI- and TDI-based polyurethanes to discolor (Wilhelm et al. 1998). The reaction mechanism for MDI-based polyurethanes is described by Wilhelm et al. 1998. The degradation reaction starts at the methylene group centered between the phenyl groups in the polymer backbone.

Irradiation using wavelengths greater than 300 nm of a polyurethane containing ester linkages (see figure 4) causes radical formation and oxidation at the methylene group in the -position to the urethane linkage and eventual scission of the polymer backbone (Wilhelm and Gardette 1997). The reaction mechanism includes peroxide formation. At 254 nm scission of the both the N-C bond and the O-C bond of the urethane linkage occurs (Wilhelm and Gardette 1997).

Photooxidation of polyether-based polyurethanes starts with oxidation of the ether component, while the urethane linkage is attacked in the second phase (Wilhelm and Gardette 1998). The ether linkage is very sensitive to photooxidation, while the urethane linkage is more stable. At the ether linkage formation of formates takes place. The formates decompose to form low molecular weight products such as ethylene ($H_2C=CH_2$), methyl formate ($HCOOCH_3$) and carboxylic acids ($RCOOH$). Once the ether linkages have disappeared, the methylene in the -position to the

nitrogen in the urethane linkage is oxidized leading to the formation of carboxylic acids and primary urethanes.

Polyurethanes containing ester linkages may react with water leading to scission of the polymer chain and formation of a polymeric acid and a polymeric alcohol (Salazar et al. 2003). The reaction is acid-catalyzed which means that since it produces an acid, it is autocatalytic and can produce runaway degradation. Since the reaction is reversible, re-esterification of hydrolytically damaged ester-based polyurethanes is at least theoretically possible.

The urethane linkage itself is also sensitive to alkaline hydrolysis (Harper and Petrie 2003 p. 269).

3.2 The effect of ageing on surface treatment properties

The degradation processes affect the characteristics that make a surface treatment effective. The effectiveness of a surface treatment system depends on its initial characteristics and on its ability to maintain those characteristics over a period of time. The most important characteristics, when it comes to protecting concrete against chloride ingress and carbonation, are water absorption, water vapor permeability, carbon dioxide permeability, crack-bridging ability and adhesion.

Chemical ageing due to temperature and light typically results in chain rupture in the polymer binder, in which case the polymer softens, and crosslinking or chain growth in which case the polymer becomes hard and brittle (Harper and Petrie 2003 p. 24). Both processes of chain rupture and linkage may proceed simultaneously.

Vipulanandan and Liu (2005) studied two polyurethane coatings over a time period of five years. They give no information about the type of polyurethane that was used. The performance of the coatings depended on the moisture content in the substrate at the time of application, see table 7. The study showed that initial high adhesion values are not necessarily good predictors for long term adhesion.

Table 7. Adhesion of two polyurethane coatings applied to the inside wall of concrete cylinders and subjected to 0.1 MPa hydrostatic pressure, simulating 10 m of groundwater, from the outside. The time of measurement is given in parentheses. Based on data from Vipulanandan and Liu (2005, figure 4).

Coating			Application conditions	Adhesion [MPa]	Adhesion [MPa]
Type	Thickness [mm]	Shore D			
PU 1	1.1	67	Dry concrete	> 2.6 (1 month)	> 1.1 (24 months)
			Wet concrete	0.9 (1 month)	0.05 (24 months)
PU 2	4.7	78	Dry concrete	0.1 (6 months)	0.15 (24 months)
			Wet concrete	1.1 (6 months)	0.7 (24 months)

In a similar study to the one performed on polyurethanes (Vipulandan and Liu 2005) four epoxy coatings were tested on the inside of concrete cylinders subjected to hydrostatic pressure from the outside (Liu and Vipulanandan 2005). The tests were performed over a time-period of almost two years, see table 8. The adhesion strength of all coatings in the study increased during the initial approximately 10-12 months after application, followed by a period of decrease. Coatings A, C and D performed roughly the same regardless of the moisture content in the concrete at the time of application, while coating B showed slightly lower adhesion upon dry application. The study

did not include information about the type of epoxies that were used or investigate the reasons for the observed loss of adhesion after the initial period of increased adhesion.

Table 8. Adhesion of four epoxy coatings applied to the inside wall of concrete cylinders and subjected to 0.1 MPa hydrostatic pressure, simulating 10 m of groundwater, from the outside. The time of measurement is given in parentheses. Based on data from Liu and Vipulanandan (2005, figure 3).

Coating			Application conditions	Adhesion [MPa]	Adhesion [MPa]
Type	Thickness [mm]	Shore D			
Epoxy A	2.0	70	Dry concrete	1.1 (7 months)	> 1.3 (15 months)
			Wet concrete	1.5 (7 months)	> 1.7 (16 months)
Epoxy B	1.5	73	Dry concrete	0.5 (1 month)	0.2 (19 months)
			Wet concrete	0.7 (1 month)	0.8 (19 months)
Epoxy C	2.0	71	Dry concrete	0.9 (7 months)	1.0 (14 months)
			Wet concrete	0.8 (4 months)	1.2 (17 months)
Epoxy D[1]	1.5	72	Dry concrete	1.2 (6 months)	1.3 (21 months)
			Wet concrete	0.8 (6 months)	1.8 (12 months)

1) Fibre-mat reinforced epoxy.

Seneviratne et al. (2000) performed field tests on the performance of three coatings in an urban outdoor UK environment. The tests lasted for five years. The study reports on the moisture levels in the concrete, adhesion between concrete and coating and on the glass transition temperatures for the coatings, see table 9. The epoxy/acrylic coating was better able to maintain a relatively constant humidity level in the concrete substrate than the other two coatings. The relative humidity of the concrete coated with acrylic/acrylic remained below 80 % during most of the test period. The relative humidity of the concrete coated with the other two coatings increased and decreased in the same manner as humidity level the uncoated specimen although at a somewhat lower level of relative humidity.

Seneviratne et al. (2000) suggest that the small cracks that appeared in the surface of the acrylic-siloxane/acrylic coating is due to its high glass transition temperature, because polymers tend to become brittle when the temperature in the environment falls below the glass transition temperature. As temperatures in Britain rarely fall below -10 ºC, brittle failure due to low temperatures is less likely in the two coatings with glass transition temperatures in the region below the minimum outdoor temperatures. The authors also suggest that a moderate adhesional bond to the substrate and ability to maintain the elastomeric properties of the coating over the temperature range in the service environment is favorable, since the coating is then better able to tolerate stresses due to movements in the substrate.

Table 9. Field tests of three coatings in an urban outdoor UK environment. Based on data from Seneviratne et al. (2000, table 2 and figure 4).

Coating type		Glass transition temperature, T_g, [ºC]		Adhesion [MPa]	
Primer	Top coat	Initial	4 years	Initial	4.5 years
Acrylic/siloxane	Acrylic	-1.0	-2.2	1.9 ± 0.12	0.9 ± 0.55
Acrylic	Acrylic	-11.0	-11.0	0.7 ± 0.48	0.5 ± 0.20
Epoxy	Acrylic	-20	-10.0	0.8 ± 0.17	1.4 ± 0.58

Al-Zahrani et al. (2002) investigated the water absorption and chloride permeability of coatings subjected to wetting/drying cycles or heating/cooling cycles. Four different coatings were studied: A polymer modified cement based coating designed to stop salt ingress, a cement based coating designed for water retaining structures, a polyurethane coating system consisting of an epoxy barrier, interlaminar primer and polyurethane coating and an epoxy system consisting of an epoxy sealer and an epoxy coating, see figure 8 and 9. The study showed that the polymer based coatings studied performed overall better than the cement based coatings. The wetting/drying cycles and the heating/cooling cycles affected the performance of the coatings differently. Wetting/drying cycles were more detrimental than heating/cooling cycles to the adhesion of the epoxy/PU coating but affected the cement coatings almost equally.

The authors (Al-Zahrani et al. 2002) conclude that the water absorption is the simplest predictor of protection against chloride induced corrosion. However inspection of the data presented shows that some care needs to be taken when using water absorption in the untreated coating as predictor. Generally treatments with low water absorption gives lower chloride permeability than treatments with high water absorption, but there are some exceptions. The specimens treated with a cement based product and the uncoated specimens had almost equal water absorption, but the chloride permeability of specimens treated with the cement based product was much lower than that which was found in the untreated specimens. Adhesion of the coatings to the untreated specimens was no predictor at all for the development of chloride permeability upon ageing. The chloride permeability of the polymer coatings were almost unaffected by both ageing schemes, whereas the chloride permeability of both cement coatings increased. All coatings had initially low chloride permeabilities, i.e. initial chloride permeability is not necessarily a good predictor of the chloride permeability for an aged coating. The same holds true for the relation between water absorption of an unaged coating compared to an aged coating. No tests were performed or explanations offered for the observed performance trends.

Schueremans et al. (2007) has reported on the findings from a field study of a quay wall at Zeebrugge Harbor performed starting in 1993. The effectiveness of treating a newly constructed wall with isobutyltriethoxysilane was evaluated after three, five and twelve year's site exposure by measuring penetration depth of the silane, chloride ingress depth and carbonation depth. The results were compared to the results obtained at an untreated wall. It was found that treatment with isobutyltriethoxysilane reduced chloride ingress significantly both above and in the tidal zone, see table 10. However the carbonation depth increased in the treated areas. The lower carbonation depth in the untreated areas may be due to rainwater blocking the pores and thereby hindering the diffusion of carbon dioxide (Yoon et al. 2007). In the areas treated with a hydrophobing agent, rain water is kept from entering the pores and the diffusion resistance is lowered (Janz and Byfors 2004).

Table 10. Chloride ingress, carbonation depth and isobutyltriethoxysilane penetration depth in concrete specimens from a quay wall at Zeebrugge Harbor. Measurements made in 2005 after 12 year's site exposure. Data from Schueremans et al. (2007, tables 4-5 and figures 8-11).

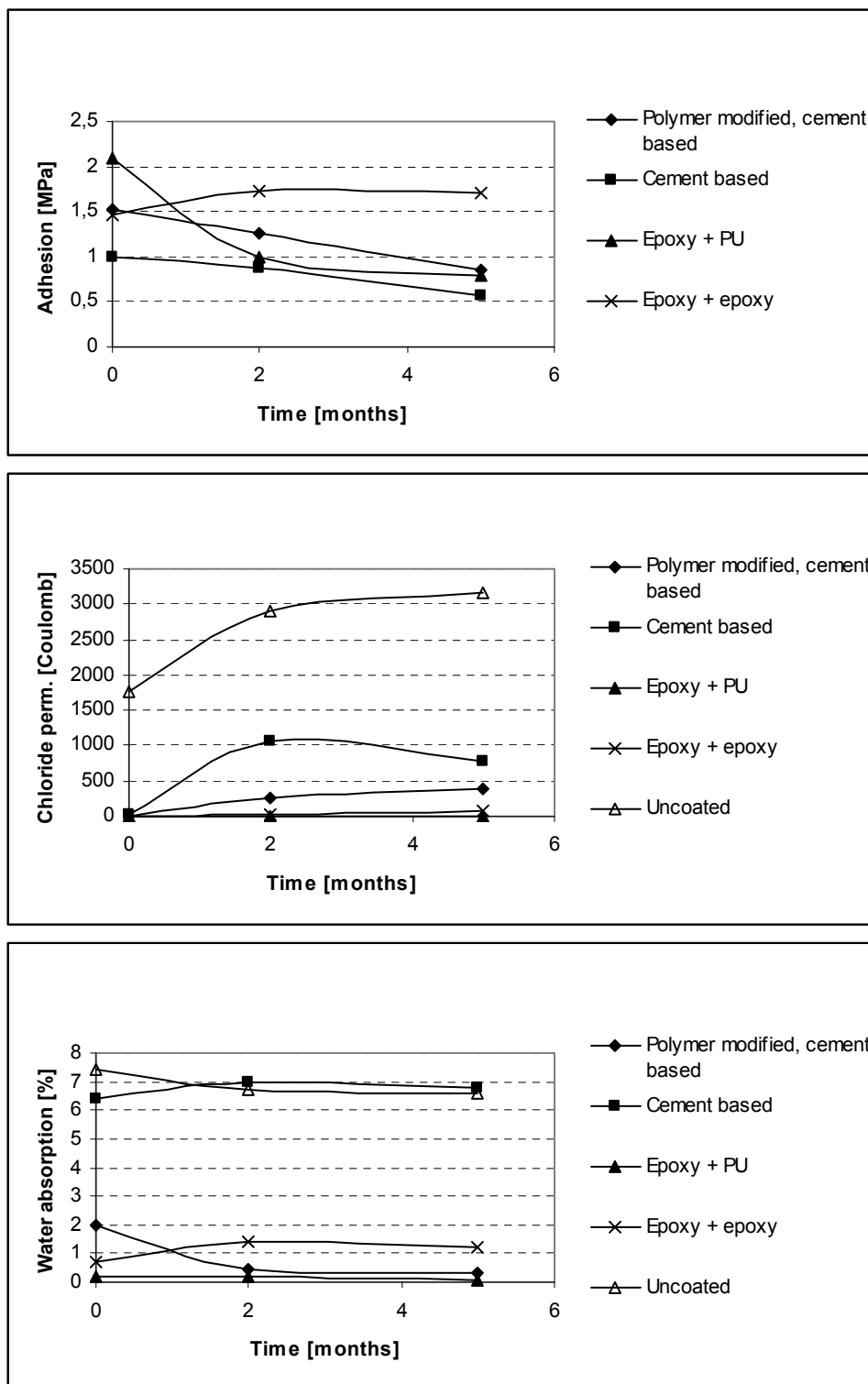| Treatment	Location	Water soluble chloride content [% Cl⁻/cem]		Carbonation depth [mm]	Silane penetration depth [mm]
		5 mm depth	45 mm depth		
Untreated	Above tidal zone	2.1	1.5	0	-
Isobutyltriethoxysilane	Above tidal zone	0.7	0.1	8-12	4-6
Untreated	In tidal zone	2.1	1.3	0	-
Isobutyltriethoxysilane	In tidal zone	0.7	0.1	4-6	5-6

Figure 8. Effect of wetting/drying cycles on the performance of coatings. Each wetting cycle consisted of 24 h submersion in water followed by drying at room temperature for 24 h. The concrete was prepared with 370 kg/m^3 of Type I cement and a water-cement ratio of 0.45. The figure is based on data from Al-Zahrani et al. (2002).
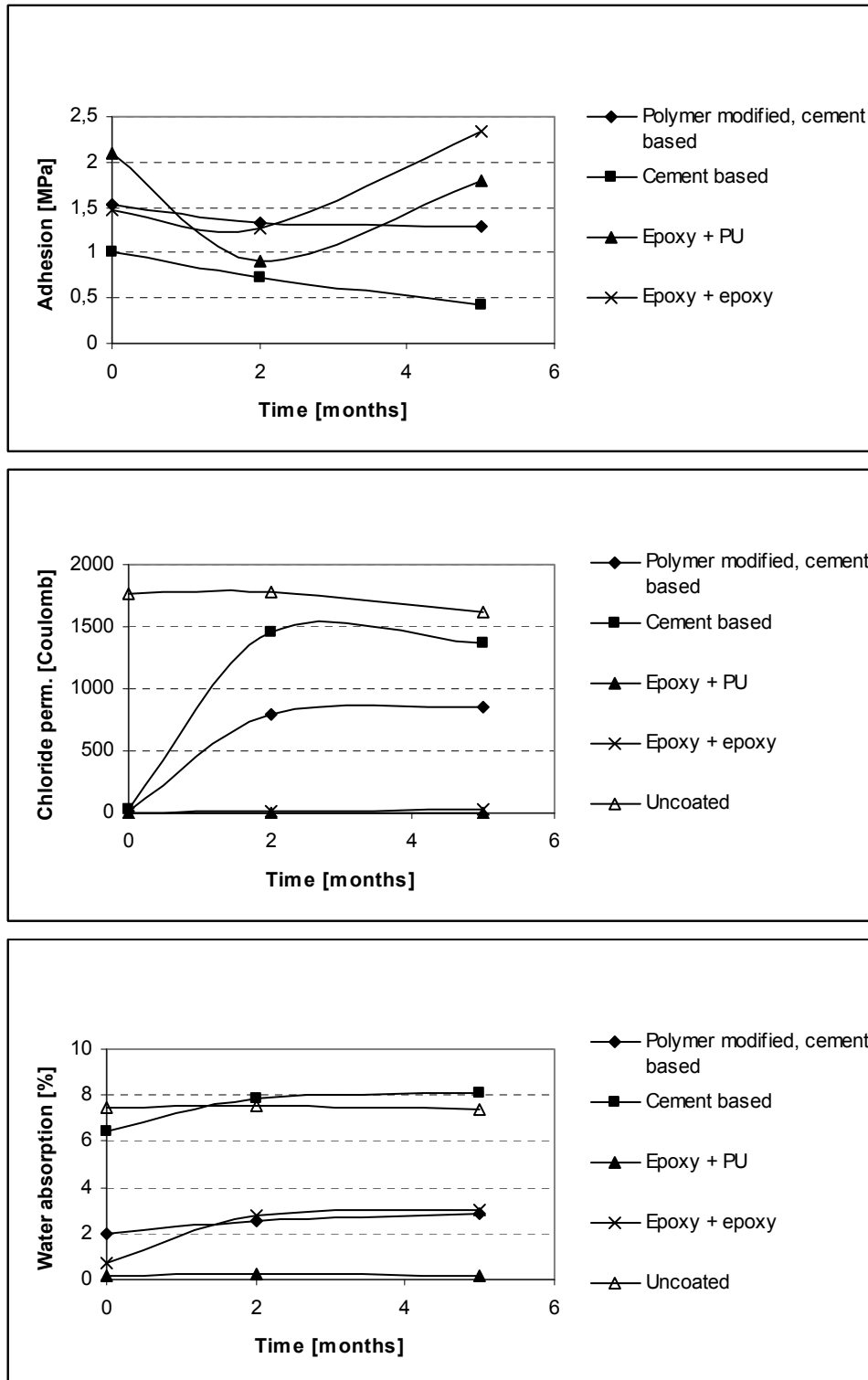
Figure 9. Effect of heating/cooling cycles. Each heating/cooling cycle consisted of 8 h at 70 ºC followed by 16 h at room temperature. The concrete was prepared with 370 kg/m^3 of Type I cement and a water-cement ratio of 0.45. The figure is based on data from Al-Zahrani et al. (2002).

3.3   The effect of climate change on ageing

The global average surface temperature is projected to increase 05-2.5 degrees by 2020-2029 and 1-6 degrees by 2090-2099 (IPCC 2007). Precipitation is projected to increase with 5-20 % for the period 2090-2099 compared to 1980-1999 for northern Europe. CO_2 concentrations has increased from a pre industrialization level of 280 ppm (atomic) to 379 ppm in 2005, and is estimated to rise to approximately 700 ppm at the end of the 21st century (IPCC 2007, Yoon et al. 2007). Climate change in the direction of more moisture and higher temperature, as predicted by IPCC for northern Europe, and steadily increasing carbon dioxide levels may enhance the deterioration speed of coatings but also put new demands on the protective ability of coatings.

3.3.1   Increased CO_2-levels

As the carbonation rate is dependent on the CO_2 concentration, Yoon et al. (2007) has investigated the effect of rising CO_2 concentrations on the carbonation depth and compared this to predicted carbonation depth assuming a constant CO_2 concentration. The projected carbonation depth for a concrete that is poured in 2000 at 60 and 100 years of age, in a sheltered outdoors area, is given in table 11. In an unsheltered area, i.e. an area where the concrete is subjected to rain the projected carbonation depth is lowered. This is because water hinders carbon dioxide diffusion. Increased rainfall may counteract the predicted increase in carbonation depth, but this effect was not taken into consideration. The effect of projected surface temperature increase on the carbonation rate was also not taken into the model. The authors conclude that it may be necessary to increase the minimum concrete coverage to reduce the risk of carbonation and rebar corrosion.

Table 11. Projected carbonation depth for a concrete poured in 2000 assuming increasing or constant CO_2 concentrations (Based on data from Yoon et al. 2007, figure 7). The calculations assumes a sheltered outdoors area.

Year	W/C 0.45		W/C 0.50		W/C 0.55	
	Constant CO_2	Increasing CO_2	Constant CO_2	Increasing CO_2	Constant CO_2	Increasing CO_2
2000	0 mm	0 mm	0 mm	0 mm	0 mm	0 mm
2060	8 mm	9 mm	10 mm	13 mm	14 mm	17 mm
2100	9 mm	13 mm	12 mm	17 mm	17 mm	23 mm

No studies could be found on the effect of climate change and carbon dioxide levels on the effectiveness of coatings to protect the substrate.

3.3.2   Ozone depletion and increased UV-B levels

Ultraviolet radiation is divided into several regions depending on their wavelength. UV-A occupies the 400-320 nm range while UV-B occupies the 320-280 nm range. Stratospheric ozone depletion is causing an increase in the amount of ultraviolet radiation reaching the surface of the Earth (Andrady et al. 2003 and 2007). Particularly UV-B has a highly damaging effect on polymers and an increase in UV-B levels may shorten the lifetime of coatings. Many studies on the effect of ultraviolet radiation on polymeric materials exist, however the effect of increased UV-B has received little attention.

4 Conclusion

Both laboratory experiments and field studies confirm that surface treatments will reduce chloride ingress and hinder carbonation. The studies show that a number of products, belonging to a number of generic product types, exist that protects the concrete substrate. However within in each generic type there are efficient as well as less efficient products. The reviewed studies rarely give information on the formulation of the surface product beyond the generic classification, and they do not necessarily provide information about the product properties that are important such as adhesion, carbon dioxide or water vapor permeability and capillary water absorption. It is therefore difficult to draw any conclusions from the studies that go beyond the obvious: some products work better than other products and many chemically very different products seem to work almost equally well. What precisely it is that makes a product work better than another, and how the better working product can be identified through tests is still an area that could benefit from more work. The reviewed literature gives little help in this respect.

It is also difficult to draw conclusions for one more reason. The test environments are generally insufficiently characterized. Given that temperature, humidity and UV radiation affects the degradation processes it is reasonable that at least these characteristics of the environment are monitored, but that is not necessarily so even in the laboratory. The meteorological conditions at the field test sites are at best ill defined, and all too often left completely to the reader's own investigative interests. Implementation of a system for characterizing the experimental environment would greatly improve the value of the performed studies. A recent study on weathering in natural and artificial environments (Deflorian et al. 2007) show that by quantifying precipitation, temperature, relative humidity, radiation and number of hours when the temperature or relative humidity is below or above critical values, it was possible to reproduce the results reasonably well in the laboratory by duplicating the conditions of the field test. This suggests that the before mentioned characteristics needs to be included in any field study. In addition more weight should be put on characterizing the surface treatments and investigating the experimental observations more thoroughly.

The review revealed the following research needs:

- **Improved and more thorough ways to classify and characterize service environments.** Field tests should be performed in well characterized environments, and the results related to the characteristics of the test environment. The relevant characteristics of the service environment must be identified.
- **Laboratory tests that are designed so that they can be related to in-field use.** This is impossible unless the characteristics of the service environments that influence surface treatment service life are better defined.
- **Studies that show the relation, if any, between initial properties and long term properties of a surface treatment.** Few studies could be found that relates initial properties and chemical composition of the surface treatment to the long-term performance.
- **In depth investigations of the mechanisms by which surface treatments fail.** Performance failures are noted but rarely investigated more thoroughly. Studies that investigate failure mechanisms in more detail would contribute towards the development of better coatings, but may also help in assessing the service life. Accelerated ageing tests are uncertain at best. It is necessary to take the failure mechanisms into account when tests are designed, and when the results are interpreted and related to field performance.

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